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An Irreversible Hydrocarbon Cell

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INTRODUCTION AND STATEMENT OF THE PROBLEM

SINCE the advent of Arrhenius' theory of electrolytic dissociation and the subsequent tendency to explain all possible phenomena as ionic, the whole subject of voltaic cells has become hopelessly involved with reactions among ions. Contemporary textbooks of electrochemistry contain, for example, such statements as these:

1. Allmand: Principles of Applied Electrochemistry, p. 87. Edward Arnold, London, 1920.

"For a chemical reaction to be carried out electrochemically, it must be of an oxidation-reduction nature, the substances taking part must be capable of ionization, and must be spatially separated, but in electrical connection."

2. LeBlanc: A Textbook of Electrochemistry, p. 261. Macmillan, New York, 1907.

"It has been seen that in all galvanic cells a reduction and oxidation take place; that is, at one electrode ions come into existence, and at the other ions disappear. (And in italics) . . . a chemical reaction between two substances can only be used as a source of electrical energy when electricity is produced or disappears during the reaction (*i. e.*, by changes in the charges of ions), and also when the two substances separated from each other are still capable of undergoing this reaction."

3. Creighton and Fink: Electrochemistry, Vol. I, p. 160. Wiley and Sons, New York, 1924.

"If a voltaic cell is to produce a continuous current it is essential that positive ions enter solution, and simultaneously, an equivalent quantity of negative ions leave solution."

* From a thesis submitted by Selma Gottlieb to the Faculty of the Graduate School of the University of Kansas in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

Our ordinary conception of reactions at the electrodes accords with these statements, and is that at the anode, for example, we may have: (1) discharge of an anion, (2) formation of a cation, (3) increase of positive charges on a cation, (4) decrease of negative charges on an anion, (5) or formation of a complex anion. We may, nevertheless, define voltaic cells as devices for the conversion of free chemical energy into electrical, made up of spontaneously and simultaneously occurring oxidation and reduction reactions which are capable of taking place at two different points and with a decrease in free energy. In the light of this definition it is apparent that the chemical phenomena capable of producing potential differences in a voltaic cell need not be limited to ionic reactions. A difference of potential is produced whenever an electrode takes up or gives off electrons, regardless of the cause. The transfer of electrons may be due to ionic reactions, but it may also be due to any other chemical reaction involving electron change, whether it concerns ions or not. We have, for instance, the entire field of organic chemistry with such reactions occurring among compounds which we certainly cannot consider as ionizing in the usual sense of the word. From theoretical considerations there is no reason why these organic oxidations and reductions cannot be made to fulfill the general conditions for a voltaic cell as stated above, since, after all, the essential feature of all oxidation-reduction reactions is electron change. In such a cell, oxidation and reduction at the electrodes would involve only electronic changes not directly concerned with the formation, discharge, or change of valence of an ion.

For such a purpose, easily oxidizable or easily reducible compounds would naturally be considered first. In this class come the unsaturated aliphatic hydrocarbons, which are particularly advantageous because of their active double and triple bonds and because of the gaseous nature of the lower members of both the acetylene and olefine series. In this work, therefore, acetylene and ethylene were used, in a cell constructed much like the usual hydrogen gas cell.

EXPERIMENTAL WORK

The ethylene used was the commercial gas obtained in metal cylinders, but the acetylene was prepared as needed by dropping lumps of commercial calcium carbide into water, thus reversing the usual process. This was accomplished by using a ten liter bottle which was closed at the top with a rubber stopper carrying a glass stopcock, and which had at the bottom another vent similarly closed.

The bottle was completely filled with water and tilted in a sink at an angle of about thirty degrees with the vertical. The stopper at the bottom was then carefully removed without allowing air to enter, lumps of calcium carbide about 1.5 cm. in diameter were dropped into the bottle at a convenient rate, and the displaced water was allowed to escape, also through the lower opening.

The electrolyte used was a molar solution of potassium chloride made by dissolved the carefully dried salt in freshly boiled and cooled distilled water. A normal calomel electrode was used rather than a saturated one in order to avoid errors due to liquid junction potentials.

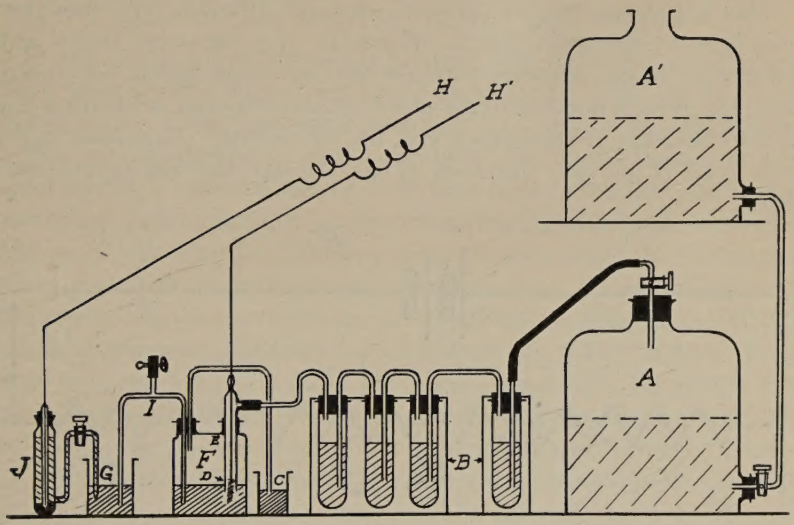

FIG. 1. Acetylene side of hydrocarbon cell.

Figure 1 shows the acetylene side of the cell; the ethylene side differed only in that the source of gas supply was a metal cylinder. The acetylene was stored in the tubulated bottle, *A*, and forced through the cell by displacing it with water flowing from a similar bottle, *A'*, placed on an elevated shelf. The first of the scrubbers, *B*, contained acid dichromate solution, the next two, 10% sodium hydroxide solution, and the last, distilled water. The electrode vessel, *E*, carrying the electrode, *D*, was supported in one neck of the Woulff bottle, *F*, from the other neck of which the salt bridge, *I*, passed to the small beaker, *G*. The calomel electrode vessel, *J*, and the salt bridge from the ethylene side of the cell also dipped into this same beaker. The beaker, *C*, served as a water trap. Connection with the electrical measuring part of the apparatus was made at *H* and *H'*.

In this cell, one Woulff bottle would have served to hold both electrodes, but it seemed desirable to avoid, in as far as possible, diffusion of gases from one electrode to the other. Because of this, each electrode had its own Woulff bottle, and the two electrodes were further separated by a small beaker of potassium chloride solution placed between the two Woulff bottles. Connection was made by salt bridges of the form shown in the figure; the electrolyte was drawn into them and held by pinchcocks on the rubber tubing. When a calomel half-cell was used, it was arranged to dip into the small beaker, *G*, and was thus presumably not contaminated by diffusion of gases from either electrode.

This apparatus was at best not air-tight although air could not pass into the electrode jacket. When the openings were sealed any differences in gas pressure between the two sides forced electrolyte from one Woulff bottle into the other, sometimes even separating one of the electrodes from contact with the electrolyte. The water traps were used to prevent diffusion of air through the gas escapement tubes.

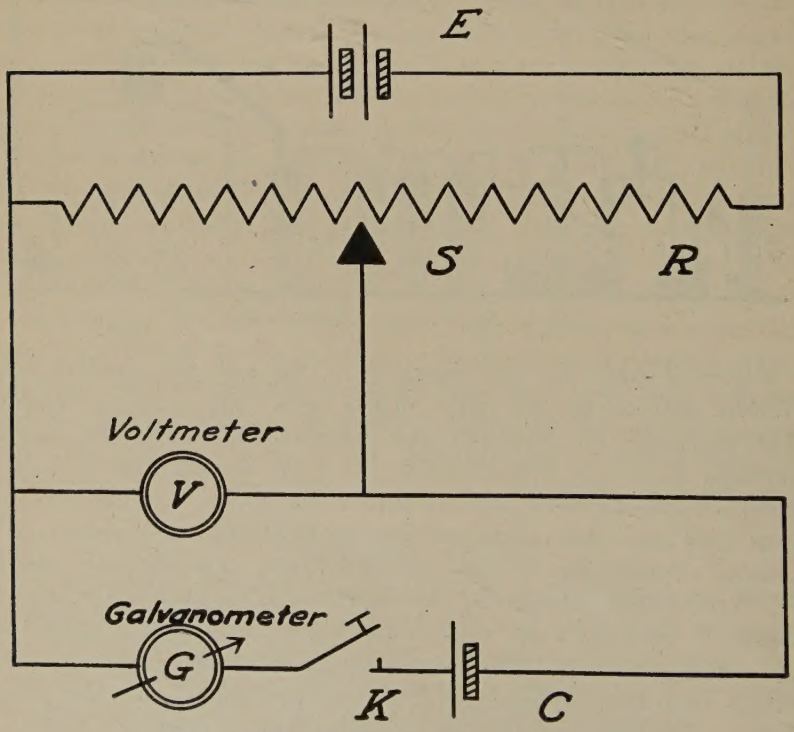

FIG. 2. Diagram of testing circuits.

Since the reproducibility of the measurements did not justify the use of a potentiometer, a simpler type of apparatus was subsituted. As shown in figure 2, the slide, S, on the resistance coil, *R*, was moved until the galvanometer, *G*, gave no deflection when the key, *K*, was depressed, showing that the electromotive force being produced in the arm containing the unknown cell, *C*, was just equal to that being shunted off the pair of dry cells, *E*, in the upper arm of the circuit. The voltage was then read directly on the voltmeter, *V*. While this is essential a potentiometric method, it does not, of course, possess the accuracy and refinement of the more delicate and more complicated apparatus.

MEASUREMENTS WITH NICKEL ELECTRODES

In the choice of electrodes, attention was naturally directed to those metals which have been found particularly useful in reactions among gases. The first work was therefore done with nickel electrodes, which always gave an electromotive force, though unfortunately not a reproducible one. It was later noted that the nickel was being slowly attacked by the potassium chloride used as electrolyte, so slowly that the effects were not visible during the time occupied by a single set of measurements, but when the electrodes were allowed to remain overnight in the electrolyte, a greenish gelatinous precipitate was present next morning. It seems rather unlikely, however, that this corrosion could have been responsible for all the difference of potential observed. A one to ten ratio of nickel ion concentrations on the two sides would account for a difference of potential of only 0.029 volt, and it seems almost inconceivable that the two gases could have been influenced the rates of attack by the potassium chloride solution to such an extent that the ratio of nickel ion concentrations on the two sides could have approached 1 to 1×10^{10}, as would be necessary to account for the difference of potential observed.

The nickel electrodes were made by wrapping nickel gauze around a wire of the same metal to make a roll about four cm. long and one cm. in diameter, and bending an end of the wire up to hold the gauze in place. The gauze rolls were corroded by dipping them into concentrated nitric acid for a moment; the green coating of nickel nitrate thus produced was converted into the oxide by heating to redness in a Bunsen flame. The oxide was then reduced by heating in a stream of hydrogen gas, and the reduced electrodes were cooled in a stream of natural gas to prevent, in as far as possible, the adsorption of

hydrogen. Since this treatment was repeated for each determination, there was always present a coating of freshly reduced nickel with a fairly large surface. With these electrodes, the readings on fifteen determinations ranged between 0.07 and 0.24 volt, with six of the fifteen values lying between 0.22 and 0.24 volt. The acetylene electrode was in every case positive to the ethylene electrode.

MEASUREMENTS WITH MISCELLANEOUS ELECTRODES

Before proceeding to a discussion of the results with platinum electrodes, it may be well to mention the work done with a variety of other substances as electrodes.

Copper electrodes were prepared by heating to redness coils of copper gauze attached to a copper wire, plunging them immediately into alcohol, and washing them in water. When these were used in the ethylene-acetylene cell, the electromotive force produced was so small that the galvanometer gave no noticeable deflection until the cell was short-circuited through it. If the electromotive force produced with nickel electrodes is to be considered due to reactions between the gases and the metal, a difference of potential should certainly be expected in the case of the copper electrodes, due to the formation of small amounts of copper acetylide.

No electromotive force was produced when the electrodes were of gold foil with a surface freshly plated from a gold cyanide solution. This inertness of the gold electrodes is of interest in connection with the later work in which platinum black was deposited on a piece of platinum foil freshly coated electrolytically with a layer of gold.

Electrodes of tungsten, iron, tin, zinc, lead, cadmium, silver and carbon were inert or practically so in this cell. Aluminum electrodes gave potentials ranging from 0.13 to 0.20 volt, but the metal was apparently being attacked by the electrolyte.

Palladium was used both in the massive form and as palladium black plated electrolytically on the smooth surface. The massive form gave an electromotive force of 0.10 volt, with the acetylene positive, but the rise to this value was very slow. The palladium black gave values ranging from 0.15 to 0.30 volt, with the acetylene positive as before.

MEASUREMENTS WITH PLATINUM ELECTRODES

Platinum black electrodes were used in a large series of experiments whose results, although not satisfactorily reproducible, are more reliable than those made with nickel, in that the platinum may safely be considered as inert. These experiments may be divided

into two groups: those made with the platinum black deposited directly on platinum foil electrodes in the usual manner, and those in which a layer of gold was interposed between the foil and the deposit. With the ordinary type of platinum black electrode, equilibrium is delayed by the fact that it must be established throughout the whole mass of platinum, including the supporting foil. With the interposition of the layer of gold, the attainment of equilibrium is hastened, since the gold serves only as an electrical conductor and does not otherwise enter into the reaction.

The gold deposit, when used, was plated from a solution containing one gram of $AuCl_3$ and two grams of KCN in 65 cc. of water. A good gold deposit was obtained only when the voltage and current density were very low; otherwise there appeared a coppery film which was not adherent.

In the first experiments, the piece of platinum foil, about 1 cm. square, was welded to a short platinum wire, which was then sealed into a piece of glass tubing. Electrical connection was made by means of a copper wire dipping into mercury in the tube. It was later considered advisable to remove any suspicion of mercury contamination of the electrodes by welding the platinum wire directly to the copper wire, thus making it possible to omit the mercury from the connection. The glass tube was of course retained for protection.

When the layer of gold was not used in preparing the platinum black electrodes, the potentials showed a marked tendency to drift, equilibrium was reached only very slowly, and attainment of the true maximum value was very uncertain. The potentials on six determinations varied from 0.19 to 0.285 volt, with the ethylene electrode positive. These values were reached in from 32 to 107 minutes.

Even when the layer of gold was interposed between the platinum foil and the coating of platinum black it was not possible to duplicate results satisfactorily, but the attainment of equilibrium was usually much more rapid. In a total of thirty-two determinations, the potentials varied from 0.20 volt with the acetylene positive to 0.52 volt with the acetylene negative. However, the ethylene was positive in twenty-four of the measurements, or 75%, and the other 25% included most of the occasions when difficulty was experienced in getting a satisfactory coating of platinum black on the electrodes.

Believing the fault to lie with the electrodes, they were introduced into the following cell,

(−)			(+)	
Pt black on Au	0.1 M-HCl H_2	M-KCl HgCl		Hg,

for which Lewis, Brighton and Sebastian* give a value of 0.3182 volt at 20° C. with a pressure of one atmosphere, using iridium electrodes instead of platinum. Since the iridium is here an inert electrode, the same value should be obtained with the inert platinum electrodes used in this work, if they were functioning properly. On eight trials, very good agreement was found with this value, using both platinum electrodes in each trial. When used in the ethylene-acetylene cell immediately after these satisfactory measurements, the electrodes gave no better results than on other occasions. Of course it is entirely conceivable that the electrodes, although in condition to catalyze the reaction, $H_2 - 2\ (-) = \text{or} \rightarrow 2H^+$, might still not be active for the reactions in which the ethylene and acetylene were involved.

In the ordinary type of voltaic cell, such as the Daniell cell, the products of the reactions are present at the start. In the case of the gas cell, the products were not known, and since they were being formed only in minute quantities during the brief time when the circuit was closed, it was impossible to determine what they were. Without any clues as to their nature, a few empirical attempts were made to find them by noting the results of adding various organic compounds to the potassium chloride electrolyte.

If we could assume that at the cathode, acetylene was being reduced to ethylene, and that at the anode, ethylene was being oxidized to acetylene, the process would be that of a concentration cell. With this thought in mind, in spite of the fact that the sign of the potential difference in 75% of the cases did not support this view, mixtures were made of one volume of ethylene to nine of acetylene and vice versa. Using these mixtures instead of the pure gases, the difference of potential was 0.05 volt, with the positive pole that concentrated with respect to the ethylene. This value, although by no means proof of the nature of the cell, is of the order of magnitude which a concentration cell would give with these concentration ratios.

An electrolyte was prepared which was molar with respect to both potassium chloride and ethyl alcohol. (It was necessary to introduce the test substance into both sides of the cell in order to avoid discrepancies on that score.) The cell in which this electrolyte was used gave an electromotive force of only 0.04 volt on one trial, but on a later attempt yielded 0.40 volt after the passage of five hours, with the acetylene positive. Still a third measurement gave only

* Jour. Amer. Chem. Soc., 39, 2245 (1917).

0.10 volt with the acetylene positive again. Results were no more satisfactory when the electrolyte was saturated with ether.

As routinely prepared, the electrodes were cleaned immediately before use by running them as cathodes in dilute sulfuric acid, and as a consequence were saturated with hydrogen. There was always then the possibility that one of the gases being passed over the platinum black displaced hydrogen from it to a greater extent than did the other, and that, as a result, the measurements actually represented a hydrogen gas concentration cell. In refutation of this, it can be stated that experiment showed the ethylene-acetylene cell to have so small a temperature coefficient that the potential was not appreciably changed even when the system was brought from room temperature to nearly 0° C. In an attempt to minimize the interference of adsorbed hydrogen, determinations were made with electrodes which had been prepared as usual but, before use, boiled in water at about 40° C. under reduced pressure to remove as much of the hydrogen as possible. Ethylene or acetylene was passed around the electrode during the process to saturate the platinum black with the gas with which it was to be used. When the electrodes were allowed to stand overnight after the dehydrogenation, the difference of potential resulting on two occasions was 0.075 and 0.115 volt with the ethylene positive. When used immediately after the dehydrogenation, the value was 0.11 volt with the ethylene negative.

Since oxygen is adsorbed by platinum black to a much less extent than is hydrogen, it seemed desirable to take advantage of the possible greater case with which the oxygen could be removed from the electrodes, by running them as anodes instead of cathodes in the dilute sulfuric acid. When used immediately after degassing, the cell gave a reading of 0.28 volt after two hours, with the ethylene positive. A second determination gave the same value, but the time was three and one-half hours. When boiled under atmospheric pressure in degassing, the cell gave only 0.075 volt, with the ethylene positive; when previously saturated with hydrogen and boiled under atmospheric pressure, the reading was 0.09 volt. Later determinations were made with the potassium chloride solutions made up separately for the two sides of the cell, one from boiled distilled water saturated with ethylene while cooling, and the other solution from water similarly treated with acetylene. The electrodes were prepared by running them as anodes in dilute sulfuric acid and degassing as described; the readings were 0.20, 0.41, and 0.33 volt, with the ethylene positive. Of these, the second value, 0.41 volt, seems

unreliable because in this case the electromotive force of the acetylene-calomel cell fell to zero and then gave a reading of 0.01 volt in the opposite direction from the previous ones.

Obviously a reversible cell should give far more definite and more reproducible values than these. The only conclusion possible from a study of these data is that we are here dealing with irreversible electrodes or with electrodes which are only partially reversible.

However, the fact that these rather considerable differences of potential were obtained indicates that reactions of some sort were taking place at the electrodes. What these reactions were cannot be stated from experimental observations, since the products were being formed only during the brief intervals when the circuit was closed by depressing the key, and then only in very minute quantities. The irreversibility of the electrodes indicates that one or more of the substances formed is a gas or a volatile liquid and is consequently lost to the cell, or that the situation is complicated by secondary reactions at the electrodes. It is entirely possible that both of these factors play a part in the phenomena within the cell.

CONCLUSIONS

1. A voltaic cell can be made with hydrocarbons as the active electrode agents.
2. The ethylene-acetylene cell is not of the concentration type.
3. The ethylene-acetylene cell is irreversible, or at best only partially reversible.